# INFLUENCE OF ENVIRONMENT ON THE RAMAN AND INFRARED SPECTRA OF QUINOLINE AND TETRALIN*

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Plate XI

**ABSTRACT.** The Raman spectra of quinoline and tetralin in the liquid state and in the solid state at −180°C and also the infrared spectra of the liquids and their solutions in some aliphatic solvents have been investigated and an attempt has been made to assign the prominent Raman and infrared frequencies of quinoline to some of the vibrational modes of the molecule.

In the solid state at −180°C quinoline exhibits a moderately strong new Raman line 49 cm$^{-1}$. On the other hand, tetralin at −180°C shows two new low-frequency Raman lines of shifts 61 and 92 cm$^{-1}$ respectively under similar conditions. It is found that some of the lines due to intramolecular modes of vibration of both the compounds undergo changes with the solidification of the liquids. The results have been compared with those due to benzene and naphthalene and it has been suggested that the changes mentioned above and the appearance of the new low-frequency Raman lines may be due to intermolecular coupling in the crystal at the low temperature.

## INTRODUCTION

It was observed by Sirkar and Ray (1960) that the crystals of benzene at −100°C show only three Raman lines in the low-frequency region and the number of these lines increases to five when the temperature is lowered to −180°C. In the case of pyridine at −180°C, however, only four such lines were observed by Kastha (1956). The increase in the number of low-frequency lines with lowering of temperature of the crystals was also observed in the Raman spectra of many substituted benzene compounds such as *p*-xylene (Biswas, 1954a), *p*-bromotoluene (Biswas, 1954b) and *m*-dichlorobenzene (Biswas, 1955). It has also been pointed out by Biswas (1957) that the number of the low-frequency lines does not depend on the shape and size of the molecule, but it depends on the nature of the substituents. In the case of naphthalene at −180°C six such lines have been observed (Ray, 1960). It would be interesting to compare the spectrum of naphthalene

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with that of quinoline, because the shapes and sizes of the two molecules are similar. Tetraline is another molecule in which one of the two rings of naphthalene has been altered by substitution. The object of the present investigation was to study the Raman spectra of quinoline and tetraline in different states in order to find out the change in the Raman spectra which might take place with change of state and also the number of low-frequency Raman lines in each case.

The infrared spectra of the two substances in the liquid state and also in solution in different solvents have also been studied in order to find out the influence of environment on the spectra.

## EXPERIMENTAL

The liquids, quinoline and tetralin supplied by the British Drug House, England, were of chemically pure quality. They were further purified by repeated distillation under reduced pressure before each exposure. The arrangements used to record the Raman spectra of the two compounds in the liquid state and in the solid state at $-180°C$ were the same as those used by Biswas (1954). An iron arc spectrum was superimposed on each spectrogram for comparison. The polarisation of Raman lines of tetralin was studied in the usual way. A Fuess glass spectrograph having a dispersion of 11 Å/mm in the 4047 Å region was used to photograph the spectra on Ilford Zenith plates. The infrared absorption spectra of the two compounds in the liquid state and in solution in $CS_2$, $CCl_4$ and *n*-heptane have been recorded with a Perkin Elmer Model 21 spectrophotometer with NaCl optics. A compensation cell was used in the reference beam in each case.

## RESULTS

The spectrograms are reproduced in Figs. 1, 2, and 3, Plate XI. The observed Raman shifts of the compounds in the liquid state and in the solid state at $-180°C$ are tabulated in Tables I and III respectively. The Raman shifts for the corresponding liquids reported by previous workers are also included in the tables for comparison. The totally polarised and depolarised lines are indicated by the letters P and D respectively written by the side of each Raman line in Table III.

The infrared spectra of quinoline in the liquid state and its solutions in $CS_2$ and in $CCl_4$ are reproduced in Figs. 4, 5(a) & (b) and 6, respectively. Also, the infrared spectra of tetralin in the liquid state and of its solutions in $CS_2$ and in $CCl_4$ are reproduced in Figs. 7, 8 and 9(a) & (b) respectively. The infrared bands of pure quinoline and its solutions in $CS_2$ and in $CCl_4$ and those of pure tetraline and its solutions in $CS_2$ and in $CCl_4$ are tabulated in Tables II and and IV respectively. The wave numbers of the bands of the pure liquids given in Landolt-Bornstein Tables are also included in the respective tables for comparison.

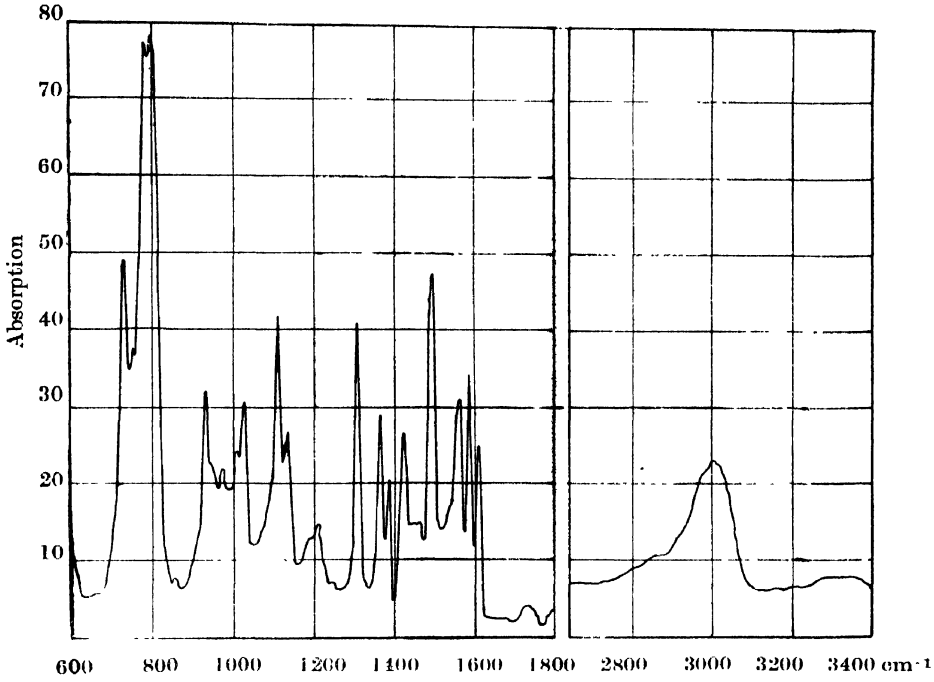


Fig. 4. Infrared spectrum of quinoline (liquid at 26°C).

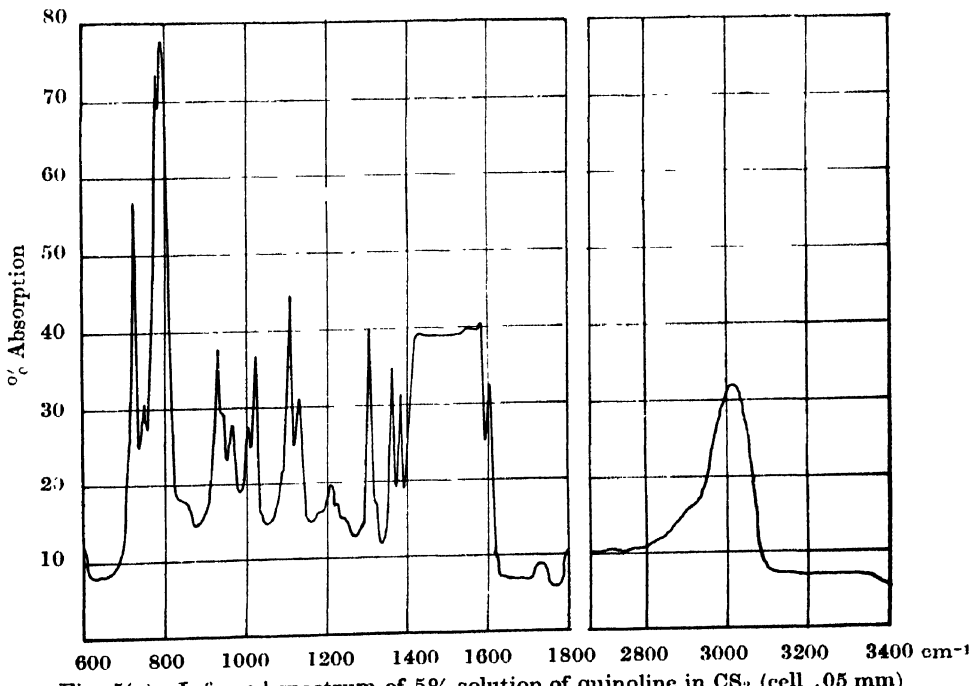


Fig. 5(a) Infrared spectrum of 5% solution of quinoline in $CS_2$ (cell .05 mm)

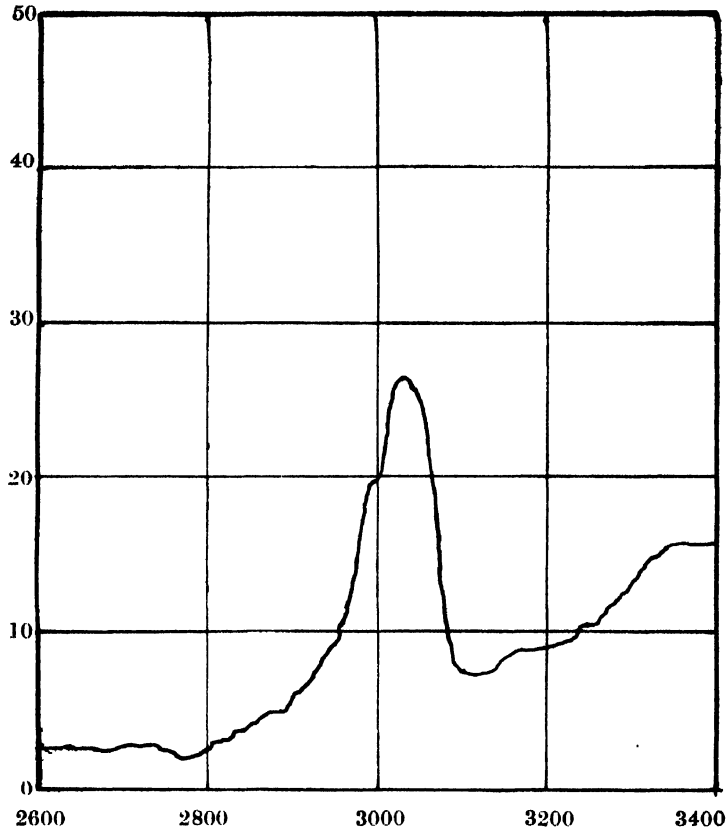


Fig. 5(b). Infrared spectrum of 15% solution of quinoline in $CS_2$ (cell .05 mm).

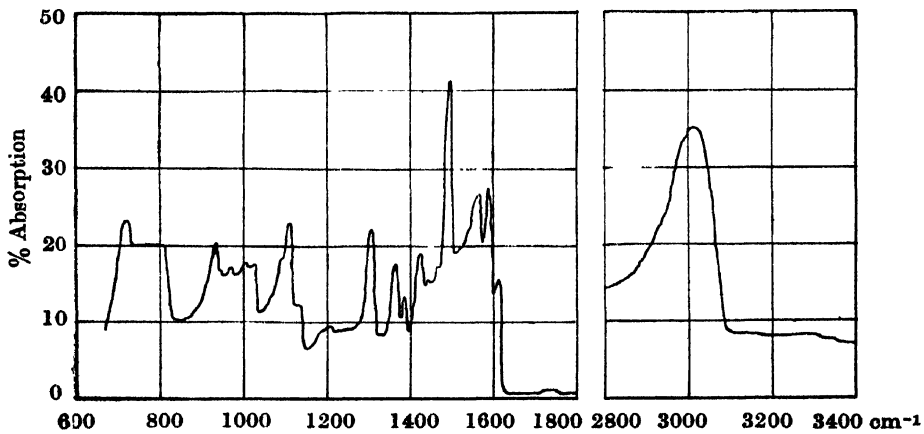


**Fig. 6. Infrared spectrum of 5% solution of quinoline in $CCl_4$.**

D :B

PLATE XI

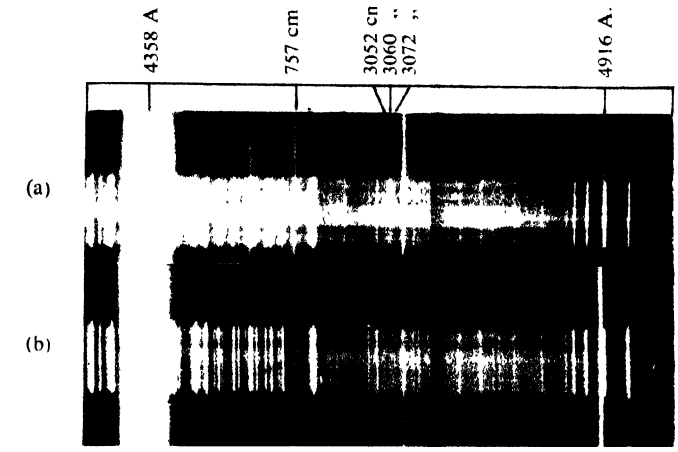


Fig.

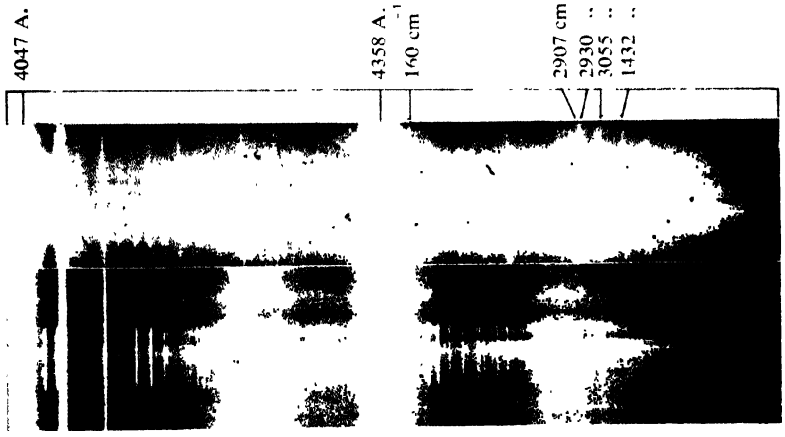


Fig. 2.

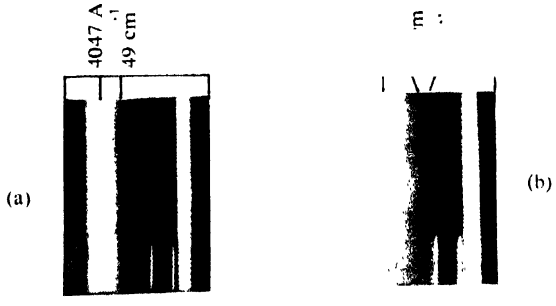


Fig. 3.

Fig. 1. (a) Raman spectrum of quinoline, liquid at 30°C
(b) ,, ,, ,, quinoline, solid at – 180°C
Fig, 2. (a) ,, ,, ,, tetralin, liquid at 30 C
(b) ,, ,, ,, tetralin, solid at – 180 C
Fig. 3. (a) Low frequency band of quinoline at – 180°C
(b) Low frequency Raman lines of tetralin at – 180°C

TABLE I

Raman spectra of quinoline—$\Delta\nu$ in c $\iota^{-1}$

| Liquid | | Solid at −180°C |
|---|---|---|
| Landolt-Bornstein Tables (1951) | Present author | Present author |
| | | 49 (2b) |
| | 191 (4b) | 190 (2b) |
| 388 (1) | 386 (4) | 384 (0) |
| 518 (5) | 519 (8) | 516 (6) |
| 701 (0) | | |
| 729 (1) | | |
| 755 (3) | 757 (10) | 751 (6) |
| 771 (1) | 776 (1) | |
| 949 (1) | | |
| 975 (0) | 963 (1b) | |
| 1008 (2) | 1013 (2) | 1014 (0) |
| 1028 (2) | 1032 (6) | 1030 (3) |
| 1113 (1) | 1117 (1) | |
| 1137 (1 | 1143 (2) | |
| 1248 (1) | | |
| 1337 (0) | 1310 (1) | |
| 1367 (6) | 1366 (15) | 1366 (12) |
| 1388 (2) | 1390 (4) | 1392 (1) |
| 1428 (3) | 1427 (10) | 1428 (4) |
| 1460 (1) | 1464 (1) | |
| 1491 (1) | 1494 (1) | |
| 1568 (4) | 1572 (10) | 1571 (4) |
| 1589 (1) | 1594 (1) | |
| 1615 (0) | 1628 (1) | |
| | 2980 (0b) | |
| 3011 (1) | 3009 (1b) | |
| | 3052 (4) | |
| 3062 (3b) | 3060 (6) | 3088 (2Vb) |
| | 3072 (2) | |

TABLE II

Infrared spectra of quinoline—ν in $cm^{-1}$

| Pure liquid | | 5% Solutions (Present author) | |
|---|---|---|---|
| Landolt-Bornstein Tables (1951) | Present author | in $CCl_4$ | in $CS_2$ |
| | 730 ms | 720 ms | 730 ms |
| | 755 ms | | 755 w |
| 782 vs | 782 vs | | 780 vs |
| 800 vs | 800 vs | | 798 vs |
| 932 s | 932 ms | 932 ms | 930 ms |
| 950 s | 950 vw | | 945 w |
| 975 ms | 975 vw | 950 vw | 970 w |
| 1005 ms | 1010 w | 970 w | 1010 w |
| | | 1005 w | |
| 1030 s | 1030 ms | 1030 vw | 1025 w |
| 1090 vw | 1090 vw | 1090 vw | 1090 vw |
| 1110 vs | 1110 s | 1110 ms | 1110 ms |
| 1135 vs | 1135 w | 1135 vw | 1135 w |
| 1185 vw | 1185 vw | | |
| 1210 vw | 1210 vw | 1210 vw | 1210 vw |
| | 1230 vw | 1235 w | |
| 1310 s | 1310 s | 1310 ms | |
| | 1365 ms | 1365 ms | 1365 ms |
| 1370 ms (b) | 1390 w | 1390 vw | 1390 w |
| 1427 s | 1427 ms | 1430 ms | 1430 ms |
| 1450 w | 1450 vw | 1445 vw | |
| 1465 w | 1465 vw | 1465 vw | |
| 1495 vs | 1495 s | 1498 s | |
| 1540 vw | 1540 vw | 1542 w | |
| 1565 ms | 1565 ms | 1560 ms | |
| 1590 ms | 1588 ms | 1590 ms | |
| 1615 ms | 1610 ms | 1610 w | |
| | 1718 vw | 1718 vw | 1730 w |
| | 1835 vw | 1835 vw | 1830 vw |
| | 1860 vw | 1860 vw | 1870 vw |
| | 1900 w | 1820 w | 1890 w |
| | 1918 w | | 1920 w |
| | 1950 w | 1950 w | 1950 w |
| | 2230 vw | | |
| | 2270 vw | | 2290 w |
| | 2310 w | 2305 w | |
| | 2340 vw | | |
| | | 2415 vw | |
| | 2840 vw | | |
| *2890 w | 2900 vw | | |
| *2930 w | | | |
| *2950 ms | | | |
| | 2980 s | | |
| *3002 ms | 3000 s | 2995 ms | 2995 ms |
| *3040 s | 3025 s | 3025 s (b) | 3025 s (b) |
| *3080 s | | | |

*Bands observed in solution in $CCl_4$

TABLE III

Raman spectra of tetralin—$\Delta\nu$ in $cm^{-1}$

| Liquid | | Solid at −180° C |
|---|---|---|
| Landolt-Bornstein Table (1951) | Present author | Present author |
| | | 61 (2) |
| | | 92 (8) |
| 113 (5) | 107 (4) D | 107 (2) |
| | | 137 (2) |
| 163 (6b) | 161 (8b) D | 158 (4) |
| 265 (4) | 262 (4) P | 265 (1) |
| 311 (1) | | |
| 435 (6) | 433 (6) P | 432 (2) |
| 457 (4) | 458 (1) D | 456 (0) |
| 511 (4) | 508 (4) P | |
| 584 (6) | 578 (6) P | 578 (3) |
| 725 (8) | 722 (12) P | 721 (10) |
| 768 (1) | | |
| 805 (3) | 804 (2) | 804 (0) |
| 816 (4b) | 819 (2) D | 819 (2) |
| 866 (3) | 869 (0) D | |
| 905 (2) | 915 (1) P | |
| 983 (1) | | |
| 1037 (10) | 1039 (12) P | 1040 (8) |
| 1067 (4) | 1064 (1b) D | 1064 (0) |
| 1116 (1) | | |
| 1159 (6) | 1162 (4) D | 1162 (2) |
| 1202 (8) | 1205 (8) P | 1206 (6) |
| 1237 (3) | 1236 (2) D | 1236 (0) |
| 1284 (3) | 1280 (8) D | 1281 (6) |
| 1343 (4) | 1337 (4b) P | |
| 1381 (1) | 1381 (1b) P | |
| 1433 (6) | 1432 (6) D | 1427 (5) |
| 1449 (3) | 1452 (2) | |
| 1581 (4) | 1576 (2) D | 1576 (0) |
| 1603 (6) | 1603 (8) D | 1603 (6) |
| 2836 (5) | 2832 (6) P | 2832 (3) |
| 2864 (6) | 2855 (3) P | 2858 (2) |
| | 2878 (3) | 2878 (2) |
| 2906 (5) | 2907 (4) | 2923 (4) |
| 2923 (4) | | |
| 2939 (6b) | 2930 (10) P | 2932 (1) |
| | | 2953 (2) |
| 3023 (3) | 3025 (5b) | 3025 (2) |
| | 3055 (5b) P | |
| 3045 (7) | | 3064 (3) |

TABLE IV

Luminescence spectra in the solid state at −180°C—$\nu$ in $cm^{-1}$

| Centres of the bands | Intensity | Separation between the two strong bands and two weak bands |
|---|---|---|
| 23690 | strong | |
| 23583 | weak | 1651 |
| 22039 | strong | |
| 21933 | weak | 1650 |

TABLE V

Infrared spectra of tetralin, ν in $cm^{-1}$

| Pure liquid | | 5% Solutions Present author | | Solutions Landolt-Bornstein Table (1951) |
|---|---|---|---|---|
| Lambert and Le Comte (1938) & Wall and McMillan (1940) | Present author | in $CCl_4$ | in $CS_2$ | in $CS_2$ |
| | | | | 580 s |
| | | | | 620 ms |
| | | | | 650 ms |
| | | | | 670 ms |
| | | | | 700 ms |
| | | | | 740 s |
| | | | | 780 s |
| 740 s | 735 vs | 730 ms | 735 vs | 805 s |
| | 780 w | | 775 w | |
| | 800 ms | | 800 ms | |
| | 810 w | 810 vw | 810 w | |
| 860 w | 860 vw | | 855 w | 855 w |
| 905 w | 895 w | 890 w | 890 vw | 890 ms |
| | 940 ms | 938 w | 940 ms | |
| | 980 vw | 980 vw | 980 vw | 975 ms |
| | 1000 vw | 1000 vw | 1000 vw | |
| | 1030 w | 1030 w | 1025 w | 1025 ms |
| | 1060 w | 1060 w | 1060 w | 1055 ms |
| 1111 w | 1105 xw | 1105 vw | 1100 w | 1102 s |
| | 1130 vw | | 1130 w | 1125 ms |
| | 1155 vw | | 1150 w | |
| | 1240 w | 1238 w | 1240 w | 1255 ms |
| | 1280 ms | 1280 w | 1280 ms | |
| | 1330 w | | 1330 w | |
| | 1350 w | 1350 vw | 1350 w | |
| 1429 w | 1430 ms | 1430 s | 1425 s | 1435 s |
| 1448 s | 1445 s | 1450 s | | |
| | 1470 ms | 1475 vs | 1470 vw | |
| | 1490 s | 1490 s | 1490 vw | |
| | 1575 vw | 1575 vw | 1570 w | |
| | 1598 vw | | | |
| | 1630 vw | | | |
| | 1640 vw | | | |
| | 1660 vw | 1660 vw | 1658 vw | |
| | 1680 vw | 1675 vw | 1675 vw | |
| | 1760 w | 1750 vw | | |
| | 1800 w | 1800 w | 1800 w | |
| | 1910 w | 1902 w | 1905 vw | |
| | 1940 w | 1935 vw | 1930 vw | |
| | 2835 s | | 2835 ms | |
| | 2890 s | 2888 s | 2890 s | |
| 2898 s | 2900 s | 2900 s | 2900 s | |
| 2975 ms | 2985 ms | 2985 ms | 2985 ms | |
| 3021 ms | 3040 ms | 3040 w | 3040 w | |
| 3058 w | 3060 w | 3060 w | 3060 w | |

## DISCUSSION OF RESULTS

### *Quinoline*

(a) *Comparison with previous work*

Table I shows that almost all the Raman frequencies given in the Tables by Landolt and Bornstein agree with those observed in the present investigation excepting the fact that the lines 191 $cm^{-1}$, 2980 $cm^{-1}$ were not reported by the previous workers and the feeble lines 701, 729, 1248 and 1337 $cm^{-1}$ have not been observed in the present investigation. Of these the line 1248 $cm^{-1}$ excited by 4047 Å line coincides with the antistokes line 519 $cm^{-1}$ excited by the 4358 Å line. There is no indication of the other faint lines mentioned above in the spectrogram obtained in the present investigation. On the other hand, the broad lines 191 $cm^{-1}$ and 2980 $cm^{-1}$ are clearly visible on the spectrogram.

(b) *Assignment of some of the Raman lines*

The quinoline molecule is similar to the naphthalene molecule, the only difference being the absence of the centre of symmetry in the former molecule. The assignment of the vibrational frequencies of quinoline to the different fundamental modes was made earlier by Ichishima (1950). More recently, several attempts have been made to assign the frequencies of the naphthalene molecules. Lippincott and O' Reilly (1955) made such assignment by comparing the Raman and infrared frequencies of naphthalene and naphthalene *d*-8. The vibration frequencies of naphthalene have been calculated by Scully and Whitfen (1960) and those of planar vibrations of the molecule have been calculated by Freeman and Ross (1960). A comparison of the infrared and Raman spectra of quinoline with those of naphthalene may be helpful in arriving at the correct assignment of the frequencies of both the molecules, and therefore, an attempt is made here to compare these results.

Two of the nine $A_g$ fundamentals of the naphthalene molecule given by Lippincott and O'Reilly (1955) do not agree with the corresponding frequencies given by Scully and Whiffen. These are 1240 $cm^{-1}$ and 878 $cm^{-1}$. These fundamentals should appear as strong Raman lines and their frequencies for quinoline are expected to be very near to those of the naphthalene molecule. Table I shows that quinoline produces intense Raman lines corresponding to fundamental frequencies 519, 557, 1032, 1366, 1427, 1572 and 3060 $cm^{-1}$. These agree fairly well with the corresponding frequencies of *g*-class vibrations of the naphthalene molecule given by Scully and Whiffen (1960). As regards the remaining two frequencies of naphthalene of this class, they have given them as 3025 $cm^{-1}$ and 1144 $cm^{-1}$, while Freeman and Ross (1960) have given them as 3004 $cm^{-1}$ and 1144 $cm^{-1}$. In the case of quinoline there is a weak line of Raman shift 3009 $cm^{-1}$ and another line at 1143 $cm^{-1}$, but there is no line of Raman shift 3025 $cm^{-1}$. Hence the assignment of the $A_g$-class fundamentals of naphthalene made by Freeman and

Ross seems to be corroborated by the appearance of corresponding frequencies of A-class vibration in the Raman spectrum of quinoline. Some of the assignments made by Lippincott and O'Reilly therefore do not seem to be correct.

As the quinoline molecule has no centre of symmetry some of the modes which are antisymmetric to the centre of symmetry in the case of naphthalene and are forbidden in the Raman effect may appear as weak lines in the case of quinoline. The line 3072 $cm^{-1}$ seems to be such a line. The infrared bands 1588 $cm^{-1}$ and 1365 $cm^{-1}$ of medium strength may correspond to the modes 1595 $cm^{-1}$ and 1387 $cm^{-1}$ of naphthalene. The strong band 1310 $cm^{-1}$ is due to a vibration which is of *u*-class in naphthalene, because the mode appears also as a weak Raman line. This may correspond to a mode $B_{1u}$ of frequency 1265 $cm^{-1}$ given by Scully and Whiffen. There are two weak Raman lines of shifts 1628 $cm^{-1}$ and 1594 $cm^{-1}$. There are no corresponding strong bands in the infrared. Hence these two lines are due probably to the modes corresponding to two $B_{1g}$ modes of naphthalene numbered 16 and 17 by Lippincott and O'Reilly (1955).

Thus in the quinoline molecule some of the vibrations of the ring have frequencies very slightly different from those of the naphthalene molecule. This difference is evidently due to the presence of the C–N bond in place of a C–C bond in the ring.

(c) *Changes in the Raman spectra of solidification*

It is observed from Table I and Figs. 1(a) & (b) and 3(a) that quinoline in the solid state at −180°C does not exhibit numerous sharp low-frequency Raman lines unlike naphthalene (Sirkar and Ray, 1950) in the crystalline state. It produces only a moderately strong band with a Raman shift of 49 $cm^{-1}$ on the Stokes side of the 4047 Å line. It was observed earlier (Kastha, 1956) that pyridine in the solid state at −180°C produces four new low-frequency Raman lines, while benzene produces five such lines under similar conditions.

In the solid state at −180°C the Raman lines 3052, 3060 and 3072 $cm^{-1}$ coalesce to form a single broad line with its centre shifted to 3088 $cm^{-1}$. Also the Raman line 757 $cm^{-1}$ corresponding to A-class vibration of quinoline shows a small shift towards the shorter wavelength region under similar conditions. All these changes suggest the formation of intermolecular linkage formed through hydrogen atoms of the neighbouring molecules in the solid state at −180°C.

(d) *Infrared spectra of solutions compared to the spectrum due to the pure liquid*

It can be seen from Table II that some bands given by previous authors appear to differ in intensity and position from those observed in the present investigation. The single broad band 1370 $cm^{-1}$ given in Landolt-Bornstein Tables appears as a doublet at 1365 and 1390 $cm^{-1}$ in the present investigation. It is observed from Figs. 4; 5(a) & (b) and 6 that the band 755 $cm^{-1}$ becomes weak in the spectrum due to the dilute solution of quinoline in $CS_2$. Moreover, the first

component of the triplet 2980 $cm^{-1}$, 3000 $cm^{-1}$ and 3030 $cm^{-1}$ due to pure quinoline seems to be weakened very much in 5% solutions in $CS_2$ and $CCl_4$ and it again appears weakly in 15% solution in $CS_2$. This shows that quinoline molecules in the liquid state are probably strongly associated and the 2980 $cm^{-1}$ band may be due to such associated molecules. The association thus breaks up in the dilute solution. The 757 $cm^{-1}$ band corresponds to the Raman line of the same vibrational frequency, but the mode being of A-Class, it is forbidden in the infrared in the case of naphthalene. It appears weakly in the case of solution of quinoline in $CS_2$ probably because in this case the centre of symmetry is disturbed by the presence of the nitrogen atom in the ring. The fact that the strength of the band increases in the pure liquid clearly shows that the centre of symmetry is perturbed to a greater extent and this also may be due to intermolecular coupling in the pure liquid mentioned above.

It can be seen from Table II that there is no strong infrared band due to C-H vibration of frequency greater than 3025 $cm^{-1}$, although naphthalene shows a strong band at 3072 $cm^{-1}$. The band at 3025 $cm^{-1}$ is to be assigned to a mode corresponding to a mode of $u$-class of naphthalene. It may correspond to the second $B_{2u}$ mode listed by Scully and Whiffen (1960). The strong bands 782 $cm^{-1}$ and 800 $cm^{-1}$ may be assigned to modes corresponding respectively to mode No. 7 of $B_{1u}$ class and No. 7 of $B_{2u}$ class given by Freeman and Ross (1960).

## *Tetralin*

(a) *Comparison with previous work*

It is observed from Table III that the doublet 2923 and 2939 $cm^{-1}$ reported by previous workers are not resolved in the present investigation and only one broad line 2930 $cm^{-1}$ has been observed. An extra line 2878 $cm^{-1}$ is also present in the spectrogram obtained in the present investigation. Regarding the other Raman lines the agreement is good excepting the lines 768 and 982 $cm^{-1}$ which are not present in the spectrogram.

(b) *Changes in the Raman spectra on solidification*

It can be seen from Table III and Fig. (3b, 2a and 2b) that tetralin in the solid state at —180°C produces two new low-frequency Raman lines of shifts 67 $cm^{-1}$ and 92 $cm^{-1}$ respectively. Of these the line 92 $cm^{-1}$ is stronger than the former one. It was previously observed (Sirkar and Ray, 1950) that naphthalene in the crystalline state produces six such lines under similar conditions. Similar comparison of the spectra due to benzene and cyclohexane shows that benzene produces five low frequency Raman lines (Sirkar and Ray, 1950) while cyclohexane does not produce any low frequency Raman line (Sirkar and Gupta, 1937). It thus appears that the presence of the six unsaturated $\pi$-electrons is necessary for the production of the low frequency lines in the case of compound

containing carbon rings. Tetralin may be regarded as a modified molecule of naphthalene with a cyclohexane ring attached to a benzene ring. Hence the diminution in the number of low frequency Raman lines in the case of the solidified tetralin at −180°C may be attributed to the diminution in the number of benzene rings in the molecule.

(c) *Other changes in the Raman spectra*

It can be seen from Table III that the Raman line 161 $cm^{-1}$ which probably corresponds to a $B_{3u}$ mode in naphthalene (Scully and Whiffen, 1961) is split up into two lines 137 $cm^{-1}$ and 168 $cm^{-1}$ respectively when the compound is solidified and cooled to −180°C. The Raman line 1432 $cm^{-1}$ which is due to C–H bending mode also shows a small shift towards the shorter wavelength region in the solid state at −180°C. The line 2907 $cm^{-1}$ shifts to 2923 $cm^{-1}$ and the line 2930 $cm^{-1}$ which is due probably to aromatic C–H stretching mode is split up into two components at 2932 and 2963 $cm^{-1}$ with the solidification of the liquid. Further, the line 3055 $cm^{-1}$ shifts to 3064 $cm^{-1}$ at the low temperature. On the other hand, the lines 2832, 2855 and 2878 $cm^{-1}$ remain unchanged at the low temperature. This shows that the C–H stretching vibrations in the $CH_2$ group remain unaffected while these due to C–H group in the ring undergo changes with solidification.

These changes suggest that probably some weak intermolecular coupling is formed in the frozen state of the substance at −180°C and the low-frequency lines may also be attributed to such coupling.

(d) *Luminescence spectra*

It can be seen from Figs. 3*a* and 3*b* that tetralin in the liquid state exhibits strong continuous luminescence, which with lowering of temperature at −180°C, appears as four discrete bands with centres at about 21933, 22039, 23583 and 23690 $cm^{-1}$ respectively as shown in Table IV. In the case of quinoline, no such bands have been observed in the solid state at −180°C. The separations of the two strong bands and two weak bands are 1651 and 1650 $cm^{-1}$ respectively. This difference may correspond to the wave number 1680 $cm^{-1}$ assigned to a $B_{3u}$ mode of naphthalene (Lippincott and O'Reilly, 1955). Probably, this type of vibration makes the triplet→singlet electronic transition partially allowed, so that the emission of the fluorescence bands takes place in the solid state at -180°C.

(e) *Infrared spectrum of solutions compared with the spectrum due to pure liquid*

Table V shows that the infrared bands due to pure tetraline reported by previous workers agree closely with those observed in the present investigation. It can also be seen from Table V that some of the infrared bands of solution of the liquid in $CS_2$ observed by previous workers differ in intensity and position from those observed in the present work. Instead of the medium strong band 1255 $cm^{-1}$ reported in Landolt-Bornstein Tables (1951), two weak bands 1240 $cm^{-1}$

and 1280 $cm^{-1}$ have been observed in the present work. Also the relative strengths of the absorption bands 855 and 890 $cm^{-1}$ reported in the Table seem to be reversed.

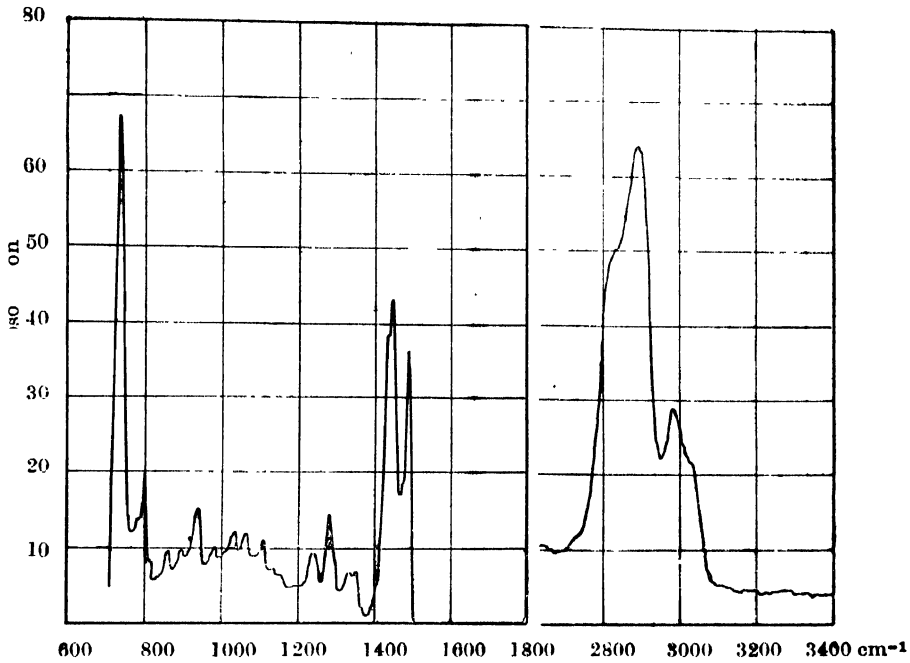


Fig. 7. Infrared spectrum of tetralin (liquid at 27°C.)

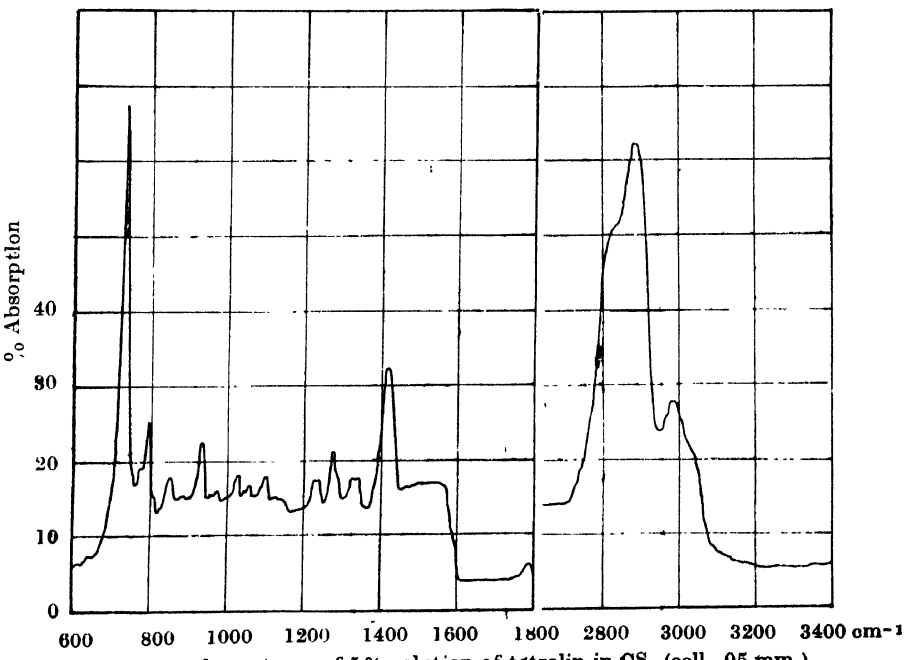


Fig. 8. Infrared spectrum of 5% solution of tetralin in $CS_2$ (cell .05 mm.)

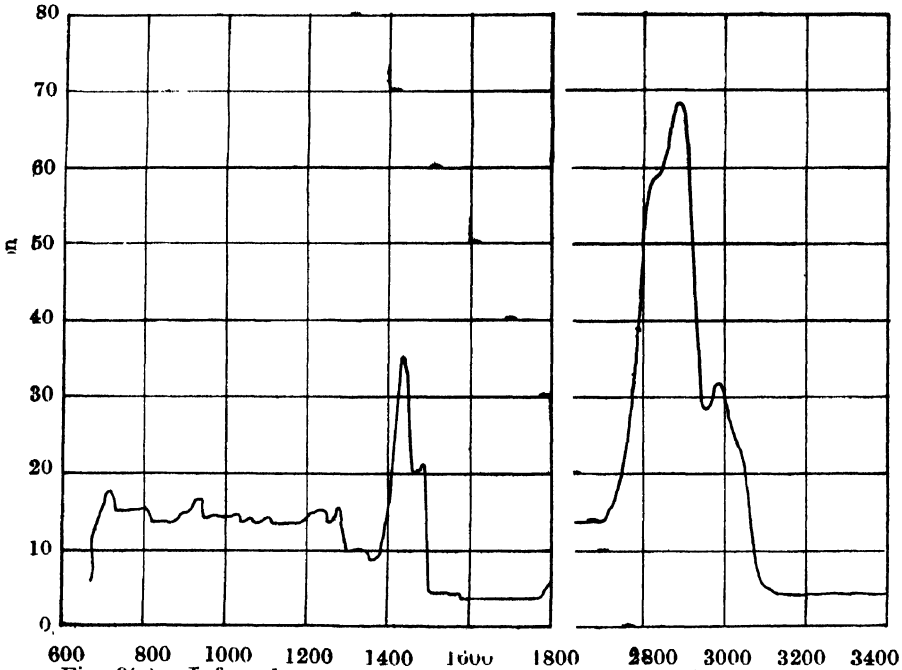


Fig. 9(a). Infrared spectrums of 5% of tetralin solution in $CCl_4$ (cell 0.5 mm).

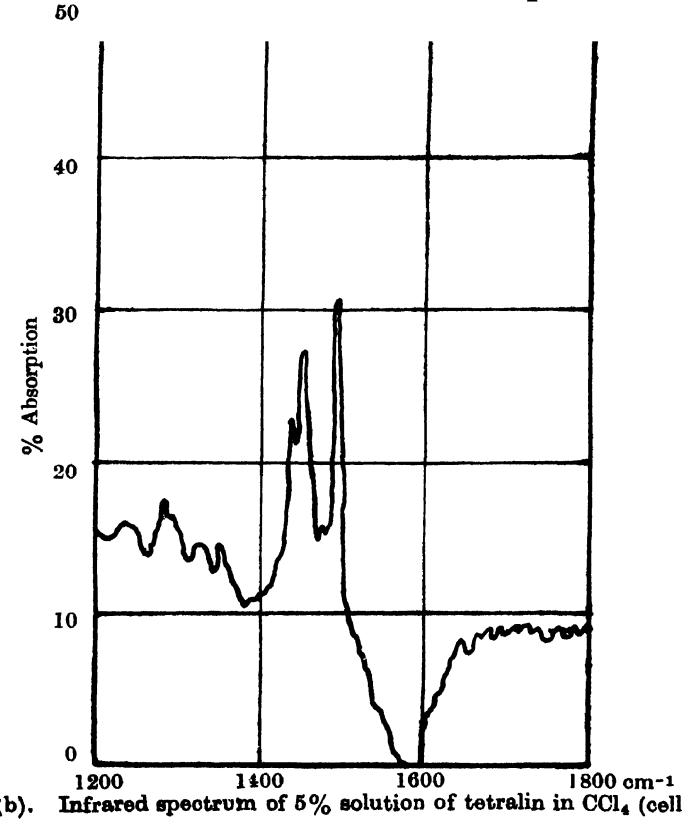


Fig. 9(b). Infrared spectrum of 5% solution of tetralin in $CCl_4$ (cell .02 mm).

It is observed from Figs. 7 and 9(a) & (b) that the relative strengths of the bands 1490 $cm^{-1}$ and 1445 $cm^{-1}$ corresponding to C-H bending modes change considerably when the substance is dissolved in $CCl_4$, the band 1490 $cm^{-1}$ being stronger than the band 1445 $cm^{-1}$ in the spectrum due to the solution while it is weaker in the spectrum due to the pure liquid. Also the bands 2835 and 2985 $cm^{-1}$, which correspond respectively to the hydrogen stretching modes in $CH_2$ and C–H groups slightly increase in strength when the substance is dissolved in $CCl_4$. No such change is observed in the case of solution in $CS_2$. So, it appears that the chlorine atoms of the solvent have some influence on the absorption due to C–H valance oscillations.

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